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(54) FLUORO RUBBER COMPOSITION AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a fluoro rubber composition capable of giving a cured article suitable for automatic loading represented by mechanization or robotization due to its excellent surface lubrication, excellent in conventional properties such as cold resistance, chemical resistance, oil resistance and the like and excellent in mechanical properties of rubber.

SOLUTION: This fluoro rubber composition comprises (A) 100 pts.wt. of a liquid perfluoro compound containing at least two alkenyl groups in the molecule and a divalent perfluoroalkylene or a divalent perfluoro ether structure in the main chain, (B) 1-100 pts.wt. of a reinforcing filler, (C) a precured base obtained by precuring a compound (C) having at least two hydrosilyl groups in the molecule capable of carrying out an addition reaction and the component (A) in a molar ratio of the hydrosilyl group of the component (C) to the alkenyl group of the component (A)=0.1-0.99 in the presence of an addition reaction catalyst, (D) 1-30 pts.wt. based on the 100 pts.wt. of the component (A), of a fluorine-containing oil insoluble in the polymer of the component (A) and (E) an effective amount of a crosslinking agent to the component (A).

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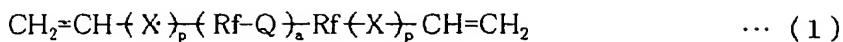
CLAIMS

[Claim(s)]

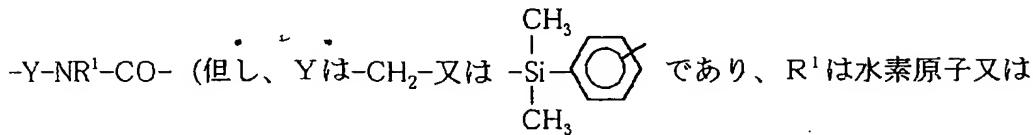
[Claim 1] (A) The liquefied perfluoro compound which has at least two alkenyl radicals in a molecule, and has divalent perfluoro alkylene or divalent perfluoro polyether structure in a principal chain The 100 weight (sections B) reinforcement nature filler The compound which contains at least two hydrosilyl radicals in the 1 – 100 weight (section C) molecule and in which an addition reaction is possible (C) -- the amount used as alkenyl radical (mole ratio) =0.1-0.99 of the hydrosilyl radical / (A) component of a component is not dissolved in the polymer of the precurve base (D) which comes to carry out precurve under existence of an addition reaction catalyst, and the (A) component -- fluorine content oil the (above-mentioned A) component 100 weight section -- receiving -- cross linking agent of the 1 – 30 weight section (E) above-mentioned (A) component Fluororubber constituent characterized by containing a bridge formation effective dose.

[Claim 2] The constituent according to claim 1 which is a compound in which the perfluoro compound in the (aforementioned A) component is shown by the following general formula (1).

[Formula 1]



[式中、Xは独立に $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{OCH}_2-$, $-\text{Y}-\text{NR}^1\text{SO}_2-$ 又は



[式中、X, p, R^1 は上記と同様の意味を示し、 R^3 は置換又は非置換の2価炭化水素基であり、 R^4 は結合途中に酸素原子、窒素原子、ケイ素原子及び硫黄原子の1種又は2種以上を介在させてもよい置換又は非置換の2価炭化水素基あるいは下記一般式(5)又は(6)

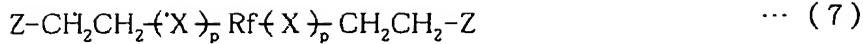


(R^5 は置換又は非置換の1価炭化水素基、 R^6 は炭素原子、酸素原子、窒素原子、ケイ素原子及び硫黄原子の1種又は2種以上を主鎖構造中に含む基)で示される基である。]

で示される基を意味し、aは0以上の整数である。]

[Claim 3] The constituent according to claim 1 or 2 which is a compound in which the compound which has at least two hydrosilyl radicals in the molecule of the aforementioned (C) component, and in which an alkenyl radical and an addition reaction are possible is shown by the following general formula (7) or (8).

[Formula 2]



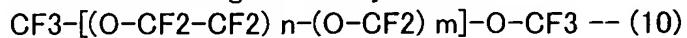
(式中、 X, p, Rf は上記と同様の意味を示す。 Z は下記一般式 (9))



(但し、 R^2 は置換又は非置換の 1 値炭化水素基、 b は式 (7) の化合物の場合は 1, 2 又は 3、式 (8) の化合物の場合は 2 又は 3 である。) で示される基を示す。]

[Claim 4] Claim 1 which is the fumed silica processed by the finishing agent to which the reinforcement nature filler of the aforementioned (B) component contains silicon in fumed silica or a molecule thru/or the constituent of 3 given in any 1 term.

[Claim 5] Claim 1 which the viscosity of the fluorine content oil which is not dissolved in the polymer of the (A) component of the aforementioned (D) component is 50-500,000cSt, and is that the molecular structure is indicated to be by the following general formula (10) thru/or the constituent of 4 given in any 1 term.



(However, n and m are integers.)

[Claim 6] Furthermore, claim 1 which blended the heat-resistant improver which used together one sort chosen from carbon black, a metallic oxide, and a metal hydroxide, or two sorts or more thru/or the constituent of five given in any 1 term.

[Claim 7] The manufacture approach of claim 1 characterized by carrying out addition mixing of (D) and the (E) component after mixing and making the - (C) component (above-mentioned [A]) react thru/or the fluororubber constituent of 5 given in any 1 term.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Without carrying out bleed out during preservation, this invention serves as a hardened material which carried out bleed out after bridge formation, and was excellent in surface lubricity, and is excellent in molding workability, and relates to the fluororubber constituent with which thermal resistance, solvent resistance, chemical resistance, low temperature-dependency-characteristics nature, and a mechanical strength give a good hardened material, and its manufacture approach.

[0002]

[Description of the Prior Art] Since the conventional vinylidene fluoride system fluororubber is the elastomer excellent in thermal resistance, chemical resistance, a mechanical strength, etc., it is industrially used in the large field focusing on an automobile and machine industry.

[0003] However, the chemical resistance is insufficient, and it swells easily in polar solvents, such as a ketone system, a lower alcohol system, a carbonyl system, and an organic-acid system, and has the fault that will deteriorate to the chemical containing an amine and rubber reinforcement and elongation will fall extremely.

[0004] Then, in order to improve those faults, the fluorine-containing Hardenability constituent which uses a perfluoro compound and a fluorine-containing ORGANO hydrogen polysiloxane as a principal component is proposed.

[0005] However, since these constituents turn into a liquefied constituent from the low polymerization degree of a perphloro compound being liquefied, although they fit a FIPG method of construction and LIMS molding, they will be inferior in workability in compression molding conventionally used by rubber molding.

[0006] Especially the production stabilized if the conventional two-sheet metal mold for rubber could not be used by frequent occurrence of the defect by molding workability and the contamination of Ayr etc. in many cases and LIMS metal mold of dedication was not newly created is difficult.

[0007] However, generally compared with the conventional two-sheet metal mold for rubber, it is expensive, and time is taken in the installation to a LIMS briquetting machine, or LIMS metal mold has troubles, like adjustment of the machine after metal mold installation takes time amount, and is unsuitable for limited production with a wide variety.

[0008] The approach of manufacturing with the fluorine-containing Hardenability constituent used as a principal component is desired [polysiloxane / the perfluoro compound and / fluorine-containing ORGANO hydroxyl] from such a background in the type rubber constituent (it is hereafter called a miltable type constituent) in which the roll activity for rubber is possible and molding by the rubber metal mold for compression molding is possible.

[0009] On the other hand, it became general to assemble in mass production method in recent years, to mechanize a process and to robotize, and being incorporated by the machine has increased rather than human being also carries a rubber workpiece. In this case, the adhesiveness on the front face of rubber checks mechanization in many cases, and clearance and lubricative grant of surface adhesiveness are called for.

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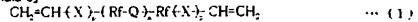
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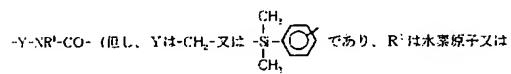
by the following general formula (1) is mentioned as this perfluoro compound.

[0017]

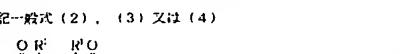
[Formula 3]



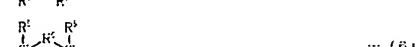
[式中、Xは独立に-CH₂-、-CH₂O-、-CH₂OC(=O)-、-Y-NR'¹SO₃-又は



置換又は非置換の1価炭化水素基)を示し、RFは2価バーフルオロアルキレン基又は2価バーフルオロポリエーテル基を示し、pは独立に0又は1である。Qは下記一般式(2)、(3)又は(4)



[式中、X、p、R'は上記と同様の意味を示し、R'は置換又是非置換の2価炭化水素基であり、R'は結合途中に酸素原子、硫黄原子、ケイ素原子及び磷黄原子の1種又は2種以上を介在させてもよい置換又是非置換の2価炭化水素基あるいは下記一般式(5)又は(6)



(R'は置換又は非置換の1価炭化水素基、R'は炭素原子、酸素原子、氮素原子、ケイ素原子及び磷黄原子の1種又は2種以上を主張構造中に含む基)

で示される基である。]

で示される基を意味し、n:10以上の整数である。]

[0018] here, it is a divalent perfluoro alkylene group or a divalent perfluoro polyether radical, as for RF, what is shown especially as a divalent perfluoro alkylene group by -CmF2m- (m=1~10 (however, j=2~6 preferably,) is desirable, and what is shown by the following formula as a divalent perfluoro polyether radical is desirable.

[0010] Although it is possible to remove surface adhesiveness easily and to raise surface slipping nature by applying a hexamethylenediamine etc. to a cast front face since a vinylidene fluoride system fluororubber has reactivity to the compound of an amine system, the above-mentioned fluorine-containing Hardenability constituent has the fault that surface treatment is difficult for the chemical stability.

[0011] When it was made in view of the above-mentioned situation and thermal resistance, solvent resistance, chemical resistance, low temperature-dependency-characteristics nature, and a mechanical strength give a good hardened material, the roll activity for rubber is possible, molding by the rubber metal mold for compression molding is possible, and this invention aims at offering the fluororubber constituent which gives the outstanding hardened material of surface lubricity, and its manufacture approach.

[0012]

[The means for solving a technical problem and the gestalt of implementation of invention] The liquefied perfluoro compound shown in (A) following as a result of inquiring wholeheartedly, in order that this invention person may solve the above-mentioned problem, (B) A reinforcement nature filler, the precurve base which comes to carry out precurve of the compound which contains at least two hydroxyl radicals in the (C) molecule, and in which an addition reaction is possible under existence of an addition reaction catalyst, (D) The fluorine content oil which is not dissolved in the polymer of the (A) component and the fluororubber constituent which comes to contain the cross linking agent of the (E) above-mentioned (A) component When thermal resistance, solvent resistance, chemical resistance, low temperature-dependency-characteristics nature, and a mechanical strength give a good hardened material, the roll activity for rubber is possible, molding by the rubber metal mold for compression molding was possible, and it found out becoming the hardened material which carried out bleed out after bridge formation, and was excellent in surface lubricity, without carrying out bleed out during preservation.

[0013] That is, by adding the fluorine content oil shown in a fluorine-containing Hardenability constituent below, when this fluorine content oil carries out bleed out to a hardened material front face after hardening, the adhesiveness on the front face of rubber is removed, and it comes to make a header and this invention for becoming the hardened material with which lubricity was given.

[0014] Therefore, the liquefied perfluoro compound which this invention has at least two alkenyl radicals in the (A) molecule, and has divalent perfluoro alkylene or divalent perfluoro polyether structure in a principal chain The 100 weight (sections B) reinforcement nature filler The compound which contains at least two hydroxyl radicals in the 1~100 weight (section C) molecule, and in which an addition reaction is possible (C) -- the amount used as alkenyl radical (mole ratio)=0.1~0.99 of the hydroxyl radical / (A) component of a component is not dissolved in the polymer of the precurve base (D) which comes to carry out precurve under existence of an addition reaction catalyst, and the (A) component -- fluorine content oil As opposed to the component 100 weight section (above-mentioned [A]) The cross linking agent of the 1~30 weight section (E) above-mentioned (A) component After mixing and making the fluororubber constituent characterized by containing a bridge formation effective dose, and the (C) component (above-mentioned [A]) react, the manufacture approach of the fluororubber constituent obtained at the process which carries out addition mixing of (D) and the (E) component is offered.

[0015] Hereafter, lessons is taken from this invention and it explains in more detail. The (A) component of the fluororubber constituent of this invention is a liquefied perfluoro compound which has at least two alkenyl radicals in a molecule, and has divalent perfluoro alkylene or divalent perfluoro polyether structure in a principal chain.

[0016] Here the perfluoro compound of the above-mentioned (A) component Compounding to resin or an amount polymer of macromolecules like rubber technically with a difficult compound Have at least two alkenyl radicals in a molecule, and it has divalent perfluoro alkylene or divalent perfluoro polyether structure in a principal chain. Preferably, the viscosity in 25 degrees C is the straight chain-like perfluoro compound which is 25~1,000,000cSt, and what is shown, for example

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[0019]

[Formula 4]

$$\begin{array}{c} \text{+CFOCF}_2\text{-}\overset{\text{r}}{\underset{\text{s}}{\text{-}}}(\text{CF}_2)_t\text{-}\overset{\text{q}}{\underset{\text{r}}{\text{-}}}(\text{CF}_2\text{OCF}_2)_u\text{-} \\ \text{X} \quad \text{X} \end{array}$$

(XはF又はCF₃基、p、q、rはそれぞれp≥1、q≥1、2≤p+q≤200、特に2≤p+q≤110、0≤r≤6の整数)

$$\begin{array}{c} -\text{CF}_2\text{CF}_2\text{OCF}_2\text{-}\overset{\text{r}}{\underset{\text{s}}{\text{-}}}(\text{CF}_2)_t\text{-}\overset{\text{q}}{\underset{\text{r}}{\text{-}}}(\text{CF}_2\text{OCF}_2)_u\text{-}\overset{\text{v}}{\underset{\text{w}}{\text{-}}}(\text{CF}_2)_z\text{-} \\ \text{CF}_2 \quad \text{CF}_2 \end{array}$$

(r、s、tはそれぞれ0≤r≤5、s≥0、t≥0、0≤s+t≤200、特に2≤s+t≤110の整数)

$$\begin{array}{c} -\text{CF}_2\text{-OCFCF}_2\text{-}\overset{\text{r}}{\underset{\text{s}}{\text{-}}}(\text{OCF}_2)_t\text{-}\overset{\text{q}}{\underset{\text{r}}{\text{-}}}(\text{OCF}_2)_u\text{-} \\ \text{X} \quad \text{X} \quad \text{X} \end{array}$$

(XはF又はCF₃基、u、vはそれぞれ1≤u≤100、1≤v≤50の整数)

$$\begin{array}{c} -\text{CF}_2\text{CF}_2\text{+OCF}_2\text{CF}_2\text{CF}_2\text{-}\overset{\text{r}}{\underset{\text{s}}{\text{-}}}(\text{OCF}_2)_t\text{-} \\ \text{w} \leq 1 \leq w \leq 100 \end{array}$$

R'として具体的には、下記のものが例がされる。

$$\begin{array}{c} -\text{C}_2\text{F}_5\text{-}, -\text{C}_2\text{F}_5\text{+}, \\ -(\text{CF}_2\text{OCF}_2)_5(\text{CF}_2\text{OCF}_2)_6-, \quad \overline{n-m}=2 \sim 200, \end{array}$$

$$-\text{CF}_2\text{CF}_2\text{OCF}_2(\text{CF}_2\text{OCF}_2)_5\text{CF}_2\text{OCF}_2\text{CF}_2-$$

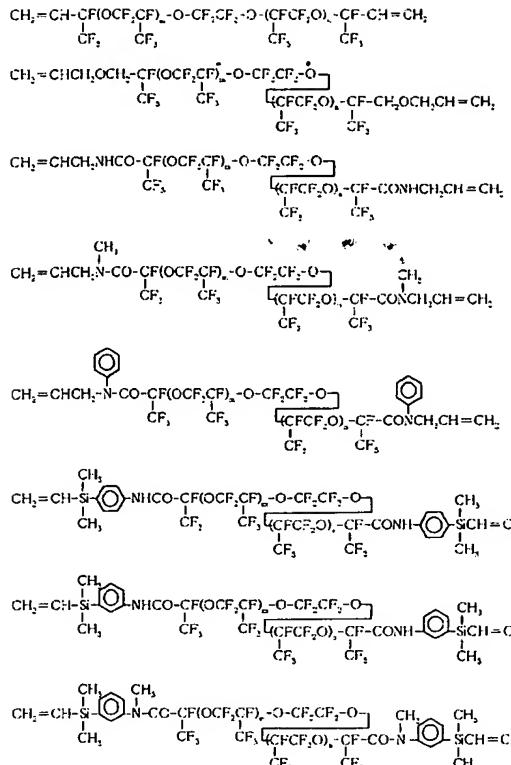
$$-\text{CF}_2\text{OCFCF}_2(\text{CF}_2\text{OCF}_2)_5\text{OCFCF}_2\text{CF}_2-$$

$$-\text{CF}_2\text{OCFCF}_2(\text{CF}_2\text{OCF}_2)_5\text{OCFCF}_2\text{CF}_2-, \quad \overline{n}=5 \sim 100, \quad \overline{m}=1 \sim 100,$$

$$-\text{CF}_2\text{OCFCF}_2(\text{CF}_2\text{OCF}_2)_5\text{OCFCF}_2\text{CF}_2-, \quad \overline{n}=5 \sim 100, \quad \overline{m}=1 \sim 100,$$

$$-\text{CF}_2\text{OCFCF}_2(\text{CF}_2\text{OCF}_2)_5\text{OCFCF}_2\text{CF}_2-, \quad \overline{n}=5 \sim 100$$

[0020] Next, Q is a radical shown by the following general formula (2), (3), or (4). [Formula 5]



[0038] As for the straight chain-like perfluoro compound of the above-mentioned (A) component, it is desirable that the viscosity in 25 degrees C is in the range of 25–1,000,000cSt, and it is especially desirable that it is 100–50,000cSt. It becomes difficult for viscosity to form the rubber hardened material which has the property satisfied at this time out of range, or there is a possibility of producing the inconvenience of workability falling.

[0039] The (B) component of the fluororubber constituent of this invention is a reinforcement

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nature filler. Although roll workability, a mechanical strength, thermal stability, weatherability, chemical resistance, fire retardancy, etc. are raised or it is added for the object, such as lowering reduction of the heat shrink at the time of hardening, decline in the coefficient of thermal expansion of the elastic body hardened and obtained, and gas permeability, this reinforcement nature filler is blended in order to mainly make it the constituent of a malleable type, and to raise roll workability and a mechanical strength.

[0040] As a reinforcement nature filler, metal carbonates, such as metallic oxides, such as fumed silica, colloidal silica, diatomaceous earth, quartz powder, a glass fiber, carbon, and ferrous oxide, titanium oxide, cerium oxide, a calcium carbonate, and a magnesium carbonate, etc. can be mentioned, and these may be processed by various finishing agents, for example. In these, the point of a mechanical strength to fumed silica is desirable, and in order to raise especially dispersibility, what was processed by the finishing agent which contains silicon in molecules, such as a silane system is desirable.

[0041] The loadings of a reinforcement nature filler are the 1–100 section to the (A) component 100 section (the weight section and the following — the same). In the less than 1 section, while the reinforcement nature of a filler falls, roll workability falls, if it exceeds the 100 sections, the flexibility of rubber will be lost, or the inconvenience of stopping coiling around a roll etc. arises.

[0042] In addition, a finishing agent may be added as an arbitration component at the time of reinforcement nature filler combination of the (B) component. A finishing agent is an arbitration component for raising the wettability between a reinforcement nature filler and a polymer, doing a combination activity easy by making reinforcement nature filler combination and distribution easy, and raising the mechanical strength of a constituent, and what contains the phloroalkyl radical or fluoropropyl alkyl ether radical which has the compatibility of the silanol group which has the compatibility on the front face of a filler, and the perfluoro principal chain of a polymer as this finishing agent in [at least one] a molecule is desirable.

[0043] Next, as a compound which contains at least two hydroxyl radicals in the molecule of the (C) component and in which an alketyl radical and an addition reaction are possible, although a hydroxyl radical is contained in what contains a hydroxyl radical in an organic compound, and an organic silicon compound, when dispersibility and thermal resistance are taken into consideration, the compound of the formula (7) shown below or a formula (8) is desirable.

[0044] [Formula 12]

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$Z-\text{CH}_2\text{CH}_2\text{X}-\text{RF}\text{X}-\text{CH}_2\text{CH}_2\text{Z}$ … (7)
 $\text{RF}\text{X}-\text{CH}_2\text{CH}_2\text{Z}$ … (8)

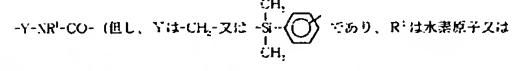
(式中、 X, p, R f は上記と同様の意味を示す。 Z は下記一般式 (9))



(但し、 R' は置換又は非置換の 1 個炭化水素基、 トは式 (7) の化合物の場合は 1, 2 又は 3, 式 (8) の化合物の場合は 2 又は 3 である。)

で示されれる基を示す。)

ここで、 X は独立に $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{OCH}_2-$, $-\text{Y}-\text{NR}'\text{SO}_3-$ 又は



置換又は非置換の 1 個炭化水素基) を示し、 R f は 2 倍バーフルオロアルキレン基又は 2 倍バーフルオロポリエーテル基を示し、 トは独立に 0 又は 1 である。

[0045] Although it is as having mentioned above about Rf, X, and p, you may differ, even if Rf, X and p in a formula (7) and (8), and Rf, X and p in a formula (1) are mutually the same.

[0046] Moreover, Z is a radical shown by the following general formula (9).



[0047] R2 is a permutation or an unsubstituted monovalent hydrocarbon radical here. As the permutation or the unsubstituted monovalent hydrocarbon radical of R2 The thing of carbon numbers 1–8 is desirable. As these radicals specifically A methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, tert-butyl, a pentyl radical, a neopentyl radical, a hexyl group, a heptyl radical, Alkyl groups, such as an octyl radical, a cyclooctyl radical, a cyclohexyl radical, Aryl groups, such as cycloalkyl radicals, such as a cycloheptyl radical, a phenyl group, a tolyl group, and a xylyl group, A part or all of a hydrogen atom of aralkyl radicals, such as benzyl and a phenylethyl radical, or these radicals A fluorine, The chloro methyl group permuted by halogen atoms, such as chlorine and a bromine, etc., a BUROMO ethyl group, a chloropropyl radical, a trifluoro propyl group, 3, 3, 4, 4, 5, 5, 6 and 6, a 6-nona fluoro hexyl group, etc. can be mentioned.

[0048] Moreover, in the case of the compound of a formula (7), in the case of the compound of 1, 2 or 3, and a formula (8), b 2 or 3.

[0049] (C) The rate of the (A) component and the (C) component is [the alkenyl radical weight in the hydroxyl radical weight / (A) component in the (C) component of the loadings of a component] 0.1 to 0.99, and the range preferably set to 0.3–0.8 in a mole ratio. It is extent which a constituent thickens somewhat as this ratio is less than 0.1, if it becomes difficult liquid rubber to work by ***ing with 2 rolls for rubber in order that a fluidity may remain and it exceeds 0.99, it will become the hardened material of rubber, and addition of a filler becomes difficult or the nonconformity of not coiling around a roll arises.

[0050] In this invention, preure of the above (A), (B), and the (C) component is carried out under existence of an addition reaction catalyst, and the preure base is obtained and let this be a combination component.

[0051] Here, as an addition reaction catalyst, a platinum metal compound is desirable. Generally a platinum metal compound is a compound of noble metals, and the platinum compound which is comparatively easy to come to hand is well used from it being an expensive rank.

[0052] As a platinum compound, although a complex, a complex with alcohol or a vinyl siloxane, platinum/silica, an alumina, or carbon of chloroplatinic acid or chloroplatinic acid, and olefins, such as ethylene, etc. can be illustrated, for example, it is not limited to these, a platinum compound — except a platinum metal — a compound — ***** — a rhodium — a ruthenium — iridium — palladium — a system — a compound — getting to know — having — *** — for example, — RhCl (PPh3) — three — RhCl — (— CO —) (PPh3) — two — RhCl (C2H4) — two — Ru — three — (— CO —) — 12 — IrCl — (— CO —) (PPh3) — two — Pd (PPh3) — four — a grade — it can illustrate.

[0053] Although especially the amount of these catalysts used can obtain the cure rate which it is not restricted and is considered as a request in the amount of catalysts, in order to obtain an economical standpoint or a good hardened material, it is good to make more preferably 0.1–1,000 ppm (platinum metal conversion) into the range of 0.1–500 ppm (same as the above) extent to the whole quantity of (A) and the (C) component.

[0054] Although the conditions of the addition reaction for the above-mentioned preure can be selected suitably and a reaction may be performed at a room temperature, for speeding up a reaction, it can heat at 100–200 degrees C, and can carry out for 10 seconds to 60 minutes.

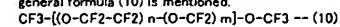
[0055] (D) The fluorine content oil of a component is the important additive of this invention, and the stability of a constituent and lubricity change with these classes and additions a lot.

[0056] Don't dissolve this fluorine content oil in the liquefied polymer of the (A) component. (A) Since a rubber degree of hardness falls and surface adhesiveness increases in order to distribute to stability that it is what is dissolved in the polymer of a component in a constituent, not to consider as bleed out and to act as a plasticizer, stop acting as a surface lubricity grant agent which is the original object.

[0057] Moreover, it is also required in a molecule to have a fluorine content radical. Since there is no compatibility with a polymer when there is no fluorine content radical, when a constituent scours, moving to a front face and carrying out bleed out is lost.

[0058] Therefore, if the requirement of the fluorine content oil of this invention is not what combines the polymer of the (A) component, a certain amount of compatibility, and non-phase solubility, it will not become.

[0059] As the concrete desirable chemical structure, what is expressed with the following general formula (10) is mentioned.



(However, n and m are integers.)

[0060] Furthermore, in addition to the above-mentioned conditions, viscosity is also important for the fluorine content oil of this invention. When the viscosity of addition oil is low, bleed out will be carried out also in the state of the constituent before hardening, the shelf life of a constituent will pose a problem, and, as for the case of hyperviscosity, the passing speed to the front face of oil will become slow. In this invention, it is desirable to carry out bleed out by the post cure after heating at the time of press molding and molding, and, as for the viscosity range, it is still more preferably desirable that it is 100–50,000cSt 50 to 500,000 cSt.

[0061] Moreover, the effectiveness of the addition of surface lubricity decreases that it is the 1–30 section and is the less than 1 section to the polymer of the (A) component, and if it exceeds the 30 sections, a mechanical strength will fall. Furthermore, it is the three to 20 section preferably.

[0062] The (E) component of this invention is a cross linking agent, and this carries out full hardening of this invention constituent thru or the (A) component. As a cross linking agent, the cross linking agent which contains a hydroxyl (E-1) radical in a molecule and in which an addition reaction is possible, or a peroxide (E-2) cross linking agent is used.

[0063] In this case, as a cross linking agent of a component (E-1), the ORGANO hydrogen polysiloxane which has preferably at least two hydroxyl radicals [three or more] can be mentioned into a molecule, and although the ORGANO hydrogen polysiloxane usually used for an addition reaction hardening mold silicone rubber constituent can be used as this ORGANO hydrogen polysiloxane, the same thing especially as the above-mentioned (C) component can be used.

[0064] The addition of this (E-1) component is sufficient amount to react with the residual alkenyl radical in the (above-mentioned A) component, and harden the (A) component. Although it is desirable to add like the conventional malleable rubber constituent from the point of preservation stability just before rubber molding as for this cross linking agent, in this case, that addition (A) When determining in consideration of the bridging material of the (C) component used when carrying out precure of the component stabilizes rubber physical properties, are important, 0.5~5, and that it is especially the range of 0.8~2 have the desirable alkenyl radical weight in the hydroxyl radical weight of the hydroxyl radical weight + (E) component in the (C) component / (A) component.

[0065] Moreover, although addition reaction catalysts, such as a platinum metal compound, can be blended with the above-mentioned (E-1) component if needed, when the addition reaction catalyst used for addition of the above-mentioned (C) component remains in the (A) component, it is not necessary to necessarily add. In addition, it is the amount of catalysts, and an addition is the same as that of the above, and is good.

[0066] On the other hand, although dibenzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, t-butyl peroxacetate, t-butyl peroxybenzoate, 2,5-dimethyl-2,5-di-t-butyl peroxyhexane, etc. are mentioned as a peroxide cross linking agent of a component (E-2), for example, the point of preservation stability or anti-scorch to 2,5-dimethyl-2,5-di-t-butyl peroxyhexane is desirable.

[0067] Although the addition of the above-mentioned peroxide cross linking agent should just be sufficient amount to stiffen the (A) component, especially its 0.5~3 section is desirable the 0.1 to 5 section to the (A) component 100 section. If bridge formation becomes imperfection if the 0.1 sections are not fulfilled, or bridge formation may become slow and exceeds the five sections, it may have an adverse effect on physical properties.

[0068] Although this invention constituent is stable enough only by containing the above-mentioned component, it may add heat-resistant improvers, such as carbon black, a metallic oxide, and a metal hydroxide, further. It is thought that these thermal-resistance improver raises thermal resistance according to the operation which absorbs or neutralizes acid, such as a radical, hydrogen fluoride, etc. which are generated at the time of heat.

[0069] Although the above-mentioned heat-resistant improver is powder, unlike the reinforcement nature filler of the (B) component, a mechanical strength is not added in order to improve, since the radical and acid which are generated at the time of heat are adsorbed or neutralized, if surface treatment is performed, surface activity will be lost and effectiveness will fall. Therefore, it is not desirable to perform surface treatment or to add to a finishing agent and coincidence.

[0070] As carbon black, although lamp black, various furnace black, acetylene black, etc. are mentioned, the anxious acetylene black of lowering of the bridge formation property by content of an impurity and rubber physical properties which is not is desirable.

[0071] As a metallic oxide, although ferrous oxide, a calcium oxide, magnesium oxide, a zinc oxide, a lead oxide, oxidation copper, titanium oxide, oxidation aluminum, cadmium oxide, cobalt oxide, cerium oxide, etc. are mentioned, if the stability within the kneading ease of being crowded to rubber, or a compound is taken into consideration, magnesium oxide, ferrous oxide, and cerium oxide can use it preferably.

[0072] As a metal hydroxide, although a potassium hydroxide, a calcium hydroxide, a magnesium hydroxide, zinc hydroxide, hydroxylation aluminum, etc. are mentioned, if the stability of a hydroxide and the safety on handling are taken into consideration, a calcium hydroxide can use it preferably.

[0073] Moreover, although these thermal-resistance improver serves as sufficient heat-resistant improvement even if it adds independently, it is using two or more components together, and the

effectiveness improves extremely.

[0074] Even if the loadings of a heat-resistant improver are the case where two or more components are used together even if it is the case where the independent activity of the one component is carried out (A) Since there is no reinforcement nature like fumed silica when there is a possibility that the effectiveness as a heat-resistant improver may decrease that the 0.01~10 section is suitable and is the less than 0.01 sections to the component 100 section and it exceeds the ten sections it may become difficult to maintain the mechanical strength of rubber. Furthermore, it is the 0.1 to 5 section preferably, and can consider as the fluororubber constituent which combines a mechanical strength and thermal resistance by this.

[0075] In the constituent of this invention, in order to raise the practicability, various additives can be added if needed. the polysiloxane (refer to JP,48-10947,B) which specifically includes the CH₂-CH(R) SiO unit (R is a hydrogen atom, a permutation, or an unsubstituted monovalent hydrocarbon radical among a formula.) added in order to control the cure rate of this constituent as these additives, and an acetylene compound (refer to U.S. Pat. No. 3445420 and JP,54-3774,B) — the iocinity compound (refer to U.S. Pat. No. 3532849) of heavy metal etc. can be illustrated further.

[0076] The production process of the fluororubber constituent of this invention consists of the third process which blends a cross linking agent, a catalyst, a bridge formation assistant, etc. of the first process which mixes and carries out precure of the (A)~(C) component, the second process which blends the oil bleeding agent of the (D) component, and the (E) component.

[0077] As equipment which mixes (A)~(C) component of this first process That what is necessary is just to use the kneader for rubber and pressurized kneader which are used for combination of common rubber, a Banbury mixer, etc. Although it is satisfactory at all in the case of these combination even if it is ordinary temperature, you may heat in the temperature requirement which a polymer does not decompose for the object, such as making shearing heat stability, and the condition has 10 minutes ~ about 8 desirable hours at 100~300 degrees C.

[0078] At this first process, it is important to increase molecular weight by making some reaction radicals of a perfluoro compound construct a bridge using a hydroxyl radical (it is called

precure), it makes it the constituent of the malleable type in which combination according a paste-like constituent to 2 rolls for rubber is possibly liquefied according to this process, and if

molecular weight is not increased at this process, the combination and ***** by the rubber covered roll will become a difficult constituent.

[0079] next, the first process which mentioned above in order for the second process to be a process which blends the oil bleeding agent of the (D) component and to make homogeneity distribute oil and last — it is desirable to blend between the processes which blend the cross linking agent of degree process etc., and even if it adds with kneading equipments, such as the kneader who uses it at the first process, it may be combination by kneading equipments, such as the 2 rolls of a final-process activity for rubber.

[0080] Moreover, especially the temperature and kneading time amount at this time should just be the proper conditions of each kneading equipment which it does not need to be careful of and oil fully distributes.

[0081] Finally the third process is the process which blends a cross linking agent, a catalyst, a bridge-formation assistant, etc. of the (E) component, and a kneader, a pressurized kneader, a Banbury mixer, etc. have the desirable 2 rolls for rubber which there is risk of the scorching phenomenon in which of bridge formation advances by mixed generation of heat, **** preferably, and can also do an activity as kneading equipment which uses at this process, and in order to suppress progress of bridge formation by generation of heat at the time of a kneading activity, it is good in what it has in cooling equipment. The kneading condition maintaining roll skin temperature at 20 degrees C or less, it does a roll kneading activity until an additive fully distributes.

[0082] Moreover, as hardening conditions for the fluororubber constituent of this invention, it is 1~30 minutes at 120~170 degrees C preferably in 100~200 degrees C for 10 seconds to 60 minutes.

[0083]

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejje

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JP,2002-188003,A [DETAILED DESCRIPTION]

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[Effect of the Invention] The fluororubber constituent of this invention fits automatic wearing of the cast which makes mechanization and robotization representation since it excels in surface lubricity, and the hardened material is excellent in the cold resistance which is the conventional property, chemical resistance, oilproof, etc., and its mechanical rubber property is also good. [0084] Moreover, since a metal mold-release characteristic also improves in order to carry out bleeding slightly also at the time of press molding, the added fluorine-containing oil contributes also to the increase in efficiency of a molding activity.

[0085] Therefore, since the elasticity of sealing materials, such as packing used for an automobile, the aircraft, space, the electrical and electric equipment, an electron, a machine, a chemical processing plant, a semi-conductor, etc. and a gasket, a diaphragm ingredient, a bulb ingredient, etc. is broadly [as required components] available, the industrial utilization range is very wide.

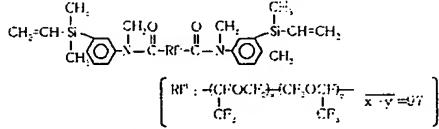
[0086]

[Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, the section shows the weight section in the following example, and viscosity is 25 degrees C in value. Moreover, the matter, each combination approach, and the assessment approach which were used in the following example are as follows.

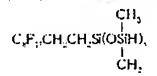
[0087]

[Formula 14]
ポリマー (ペーブルオロ化合物)

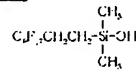
粘度4, 400cSt, 平均分子量16, 500, ビニル基量0, C13%ル, 100g



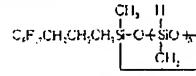
ブレキュー剤 (付加反応架橋剤)



表面処理剤



付加反応架橋剤



[0088] addition reaction catalyst PL50T and trade name by Shin-Etsu Chemical Co., Ltd. platinum compound catalyst reinforcement nature filler R976 and trade name made from

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejje

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Japanese Aerosil the fumed silica reaction control agent ethynyl cyclohexanol processed by the silicon system finishing agent, and 50% toluene solution carbon black DIN — a turnip — a rack and trade name by DENKI KAGAKU KOGYO K.K. acetylene black oil IFONBLN Z60 and AUSIMONT trade name Perfluoro polyether oil oil 2FONBLN YPL1500 and AUSIMONT trade name Perfluoro polyether oil oil 3FONBLN Y45 and AUSIMONT trade name Perfluoro polyether oil oil 4 Demunn S65, Daikin, LTD. trade name Perfluoro polyether oil oil SKF96, Shin-Etsu Chemical Co., Ltd. trade name The temperature in the pressurized kneader for the SI, trial of combination of dimethyl silicone oil base constituent 170 degrees C was raised and it added by combination as shows a polymer, a precure cross linking agent and a catalyst, a filler, a finishing agent and a heat-resistant improver in a table 1.

[0089] The base constituent was obtained for kneading continuously [the same temperature / for 1 hour] after addition termination of a filler.

The oil additive combination above-mentioned base constituent was twisted around ejection and 2 rolls for rubber from the kneader, the amount which shows various oil in tables 2 and 3 to the polymer 100 section was blended, and the last compound was obtained.

At the cross linking agent combination last, the addition reaction control agent and the addition reaction cross linking agent were blended with the above-mentioned last compound with 2 rolls for rubber, and the fluororubber constituent which can be hardened was obtained.

after creating the fluororubber constituent in which the constituent physical-properties assessment approach profit **** hardening is possible with the 75t press for rubber and creating the rubber sheet of 2mm thickness the condition for 150 degrees C and 10 minutes, 200 degrees C and the post cure of 4 hours were performed. According to the JIS rubber assessment approach, physical-properties measurement (a degree of hardness, elongation, tensile strength) was performed for this sheet.

After leaving the sheet obtained by the surface lubricity assessment above after post cure termination for 24 hours, coefficient of friction was measured using the front-face nature measurement machine (the poly recorder HEIDON, new east science incorporated company make), and the surface lubricity resulting from the bleeding of oil was evaluated.

[0090]

[Table 1]

配合	添加剤	配合量
ベース組成物配合	ポリマー	100
	ブレキュー剤	1.8
	触媒	0.2
	耐性性フィラー	35
オイル配合	表面処理剤	6
	耐熱性向上剤	1
	各種オイル	変量
架橋剤配合	架橋剤	0.2
	調滑剤	1.3

[0091] It has [examples 1~4] perfluoro polyether structure, and the variate of the oil 1 which is not dissolved in a polymer was carried out, it added to the base constituent and the rubber constituent was produced by the above-mentioned approach, and the good result was obtained when the above-mentioned approach estimated rubber physical properties and a surface characteristic for this rubber constituent. The addition and assessment result of oil are shown in a table 2. Moreover, the bleeding of oil has observed visually on the front face of a rubber molding sheet at this time.

[0092] When rubber physical properties and a surface characteristic were evaluated and the addition effectiveness of oil 2 was checked like the example 3 by the same addition number of copies as the [example 5] example 3, although it was somewhat inferior to the example 3, the

rubber sheet which has a surface characteristic with small coefficient of friction as compared with oil un-adding [of the example 4 of a comparison] was obtained. There was little oil bleeding at this time as compared with an example 3. The addition and assessment result of oil are shown in a table 2.

[0093] Although the oil 3 and 4 which has the perphloro polyether structure of resemblance in the example by the same addition number of copies as the [examples 1 and 2 of comparison] example 3 was added, rubber physical properties and a surface characteristic were evaluated and this addition effectiveness was checked like the example 3, since this oil was melted in a polymer, bleeding was not carried out to a front face and improvements of a surface characteristic were few. The addition and assessment result of oil are shown in a table 3.

[0094] Although there was no dissolution to a polymer since polymer structure was completely different silicon system oil when rubber physical properties and a surface characteristic were evaluated and the addition effectiveness of oil 5 was checked like the example 3 by the same addition number of copies as the [example 3 of comparison] example 3, since there was also no compatibility with a polymer, oil could not be moved to a front face, and bleeding was not generated. The addition and assessment result of oil are shown in a table 3.

[0095] When the assessment same about the constituent before adding [example 4 of comparison] oil as an example was performed, the constituent before adding oil had large coefficient of friction, and was what has some surface adhesiveness. This assessment result is shown in a table 3.

[0096]

[A table 2]

	測定例1	測定例2	測定例3	測定例4
(ゴムオイル)				
ゴムオイル	ゴムオイル	ゴムオイル	ゴムオイル	ゴムオイル
密度(g/cm ³)	600	600	600	630
ゴムとの接着	分離	分離	分離	分離
ゴムの吸水率 (10%水蒸気下で5分間加熱)	3	5	8	12
(ゴム物性)				
硬度(HRSH)	71	70	65	65
引張強さ(kg/cm ²)	12.1	11.7	12.0	11.2
伸び(%)	300	320	300	320
子偏強度(kg/cm ²)	21	22	21	22
(油添加量)				
添加油量	6.2	6.2	6.2	6.1

[0097]
[A table 3]

	測定例1	測定例2	測定例3	測定例4
(ゴムオイル)				
ゴムオイル	ゴムオイル	ゴムオイル	ゴムオイル	なし
密度(g/cm ³)	670	100	1000	-
ゴムとの接着	分離	分離	分離	-
ゴムの吸水率 (ゴム(100)に水蒸気を5分間加熱)	8	8	8	-
(ゴム物性)				
硬度(HRSH)	59	64	55	71
引張強さ(kg/cm ²)	12.4	12.9	10.3	12.2
伸び(%)	340	360	340	300
子偏強度(kg/cm ²)	20	21	20	23
(油添加量)				
添加油量	6.1	6.2	6.1	6.4

[Translation done.]